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AQUEOUS ALKALI RESISTANT PRINTING INK

This application is a continuation-in-part of copending Application Serial No. 09/133,484 filed August 12, 1998. This application claims the
5 benefit of United States Provisional Application Serial No. 60/055,140 filed August 12, 1997.

Background of the Invention

The invention relates to the use of a water-based latex of an acrylic modified waterborne alkyd dispersion. The hybrid resin is prepared by the
10 polymerization of at least one ethylenically unsaturated monomer, which may be a latent oxidatively functional acrylic monomer, in the presence of a waterborne alkyd having at least one pendant sulfonate functionality. Such acrylic modified waterborne alkyds are useful as vehicles in ink formulations having improved gloss and alkali resistance.

15 In recent years, considerable effort has been expended by the ink industry to develop low or zero VOC (volatile organic compound) containing inks. Regulations to limit the amount of VOC content of inks have encouraged research and development to explore new technologies directed at reducing solvent emissions from industrial printing operations
20 such as flexographic, rotogravure, letterpress, lithographic, and screen printing. One technology involves the replacement of organic solvents with water and is of particular interest for the obvious reasons of availability, cost, and environmental acceptability. However, while the move from organic solvent-based compositions to aqueous compositions brings health
25 and safety benefits, aqueous ink compositions must meet or exceed the performance standards expected from solvent-based compositions. The need to meet or exceed such performance standards places a premium on the characteristics and properties of waterborne polymer dispersions used in aqueous ink compositions.

30 Waterborne polymer dispersions have been prepared from each of the three primary industrial film-forming polymer types: polyesters, acrylics and alkyds. Of the three polymer types, alkyd resins, due to their low molecular weight, exhibit exceptional film forming ability, which translates into very high gloss in the final ink film. Resistance properties are

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developed, as with traditional solvent-borne alkyds, via autooxidative crosslinking of the alkyd film. However, while alkyd polymers have shown, and continue to show promise, they have relatively slow "dry" and/or cure times, particularly at ambient temperatures. In an attempt to address such concerns, hybrids of waterborne alkyds and relatively high molecular weight acrylic polymers have received considerable attention.

U.S. Patent 4,413,073 describes the preparation of an aqueous dispersion of particles of a film-forming polymer comprising a pre-formed polymer and at least one polymer formed in situ ("multi-polymer particles"). The dispersion is prepared in the presence of an amphipathic stabilizing compound having an HLB of at least 8 and whose lipophilic portion comprises at least one ethylenic unsaturation. The aqueous dispersion is useful as a film-forming component of coating compositions.

U.S. Patent 4,451,596 describes water-dilutable alkyd and acrylate resins for use in water-dilutable lacquer systems. A method for the preparation of water-dilutable resin preparations based upon alkyd and acrylate resins is also described.

U.S. Patent 5,567,747 describes a printing ink composed of an epoxy ester resin, an inorganic or organic pigment, a drier, a drier activator such as 2,2'-bipyridyl, a wax, and a cyclodextrin that enables lower drier levels to be used. This is a water based oxidatively cured printing ink especially suited for flexographic printing.

U.S. Patent 5,623,041 describes a polymer vehicle useful in preparing an ink or coating composition having good alkali resistance. The patent describes a water dispersible polymer of an unsaturated fatty acid functionalized acrylic. Also described is a method of coating a substrate by contacting the surface with said polymer and drying of the applied film.

European Patent Application 0 555 903 describes a water-dispersible hybrid polymer of an unsaturated fatty acid-functionalized polyester. In addition, aqueous dispersions of such a hybrid polymer for use in aqueous coating compositions with a high solids content and films produced by using such coating compositions are described.

PCT Application WO 95/02019 describes an emulsion of an air-drying resin dispersed in water and the preparation of such emulsions. Hybrid emulsions of an alkyd resin and an acrylate resin are also described.

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PCT Application WO 99/07799 describes a water-based latex of an acrylic- modified waterborne alkyd dispersion in water. The acrylic-modified waterborne alkyd is a hybrid resin prepared by the polymerization of at least one latent oxidatively functional (LOF) acrylic monomer in the presence of a waterborne alkyd.

PCT Application WO 99/07759 describes a water-based latex of an acrylic-modified waterborne alkyd dispersion in water. The latex is prepared by the emulsion polymerization of at least one ethylenically unsaturated monomer or at least one LOF acrylic monomer in the presence of a waterborne alkyd having at least one pendant sulfonate functionality whereby the latent oxidative functionality survives polymerization.

Previous alkyd-acrylic hybrid latexes for use in inks have been prepared using alkyds, which do not contain metal sulfonate groups. Further, the acrylic polymers of these previous hybrids are either non-reactive or possess reactive groups (e.g. hydroxyl groups) which react, as do similar groups present in the alkyd resin, with aminoplasts such as melamine formaldehyde resins and only at elevated temperatures. In addition, there is not been found any latexes which when used in ink formulations provide the needed alkaline resistance.

Summary of the Invention

The present invention is directed to water-based latexes of acrylic-modified waterborne alkyd resins. The acrylic-modified waterborne alkyd resins are hybrid resins resulting from the polymerization of at least one ethylenically unsaturated monomer in the presence of a waterborne alkyd having at least one pendant sulfonate functionality, i.e. a sulfonated waterborne alkyd. The invention also provides a method for preparing such water-based latexes by polymerizing a hybrid resin resulting from the polymerization of at least one ethylenically unsaturated monomer in the presence of a sulfonated waterborne alkyd. The invention further provides ink compositions containing the water-based latexes of the invention which exhibit improved alkali resistance, improved gloss, and lower solvent content.

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Detailed Description of the Invention

The invention provides water-based latexes of acrylic-modified waterborne alkyd resins and their use as ink binders. In one embodiment, the latex affords a stable, emulsion of a hybrid resin resulting from the polymerization of at least one ethylenically unsaturated monomer in the presence of a waterborne alkyd having at least one pendant sulfonate functionality, i.e. a sulfonated waterborne alkyd. In another embodiment, the latex affords a stable, emulsion of a hybrid resin resulting from the polymerization of at least one latent oxidatively-functional (LOF) acrylic monomer in the presence of a waterborne alkyd having at least one pendant sulfonate functionality such that the acrylic monomer retains a sufficient amount of LOF groups for further reaction with other LOF groups or alkyd functionality after or upon film formation. In a third embodiment, the hybrid latexes of the invention are used in the formulation of printing inks having good alkali resistance. Latexes of the invention are stable when stored at temperatures at or moderately above room temperature. The latex of the invention is capable of affecting crosslinking upon film formation. Such latex films or coatings may be cured at ambient temperature, thermally or photochemically.

In the water-based latexes of the invention, the acrylic-modified waterborne alkyd resin generally exists as particles dispersed in water. The particles are generally spherical in shape. The particles may be structured or unstructured. Structured particles include, but are not limited to, core/shell particles and gradient particles. The core/shell polymer particles may also be prepared in a multilobe form, a peanut shell, an acorn form, or a raspberry form. It is further preferred in such particles that the core portion comprises about 20 to about 80 wt% of the total weight of said particle and the shell portion comprises about 80 to about 20 wt% of the total weight of the particle.

The average particle size of the hybrid latex may range from about 25 to about 500 nm. Preferred particle sizes range from about 50 to about 300 nm, more preferably from about 100 to 250 nm. The hybrid latex particles generally have a spherical shape.

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The glass transition temperature (T_g) of the acrylic portion of the hybrid resin in accordance with the invention may be up to about 100°C. In a preferred embodiment of the invention, where film formation of the latex at ambient temperatures is desirable, that glass transition temperature may preferably be under about 70°C, and most preferably between about 0°C to about 60°C.

The acrylic-modified waterborne alkyd resins of the invention are prepared by polymerization of at least one ethylenically unsaturated monomer in the presence of a sulfonated waterborne alkyd. If at least one of the ethylenically unsaturated monomers is a latent oxidatively functional (LOF) acrylic monomer, as described below, the acrylic-modified waterborne alkyd resins of the invention may be prepared in the presence of a sulfonated waterborne alkyd such that sufficient latent oxidative functionality of the acrylic monomer survives the polymerization process to enhance crosslinking of the hybrid resin. Any polymerization process known in the art may be used. Preferably an emulsion polymerization process is used since emulsion polymerization allows for the preparation of high molecular weight polymers at low viscosity. The polymerization may take place as a single stage or multi-stage feed. If a multi-stage feed is used, one or more stages may contain an LOF acrylic monomer or mixtures of LOF acrylic monomers. Different LOF monomers may also be used in different stages. Other copolymers (non-LOF containing) may also be copolymerized with the LOF monomers. Such suitable copolymers may be selected from the list of ethylenically unsaturated monomers discussed below.

The preparation of emulsion polymers of acrylic-modified waterborne alkyd resins containing latent oxidative functionality is one possible solution for a coating composition which crosslinks under a variety of cure conditions, e.g. ambient, thermal, and photochemical.

Sulfonated Waterborne Alkyd Resin

A sulfonated waterborne alkyd resin for use in the water-based latex of the invention may be any waterborne alkyd resin having at least one pendant sulfonate functionality known in the art, including any water-dissipatable, water-dispersible, or water-reducible (*i.e.* able to get into water) alkyd resin. Examples of such alkyd resins are described in U.S. Patent

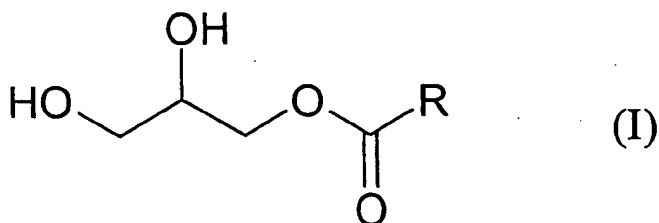
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Nos. 5,378,757 and 5,530,059, which are incorporated herein by reference. Generally sulfonated waterborne alkyd resins may be prepared by reacting a monobasic fatty acid, fatty ester or naturally occurring-partially saponified oil; a glycol or polyol; a polycarboxylic acid; and a sulfomonomer or

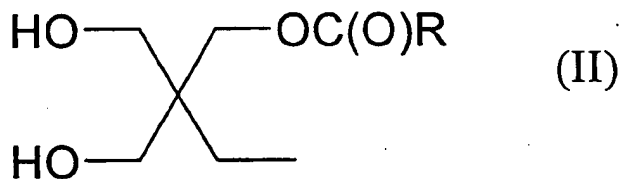
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sulfomonomer adduct containing at least one sulfomonomer group.

The monobasic fatty acid, fatty ester, or naturally occurring-partially saponified oil is preferably selected from the formulae (I), (II), and (III):



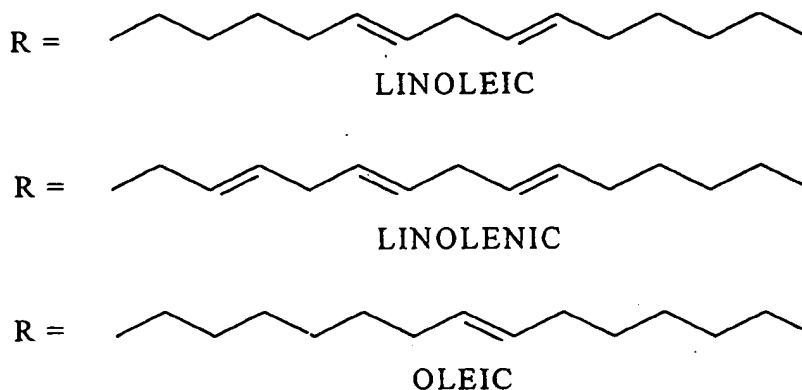
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Where the R group is a C₈-C₂₀ alkyl group. More preferably, the R group is one of the following:

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The monobasic fatty acid, fatty ester or naturally occurring-partially saponified oil is preferably prepared by reacting a fatty acid or oil with a polyol. Examples of suitable oils include, but are not limited to, sunflower oil, canola oil, dehydrated castor oil, coconut oil, corn oil, cottonseed oil, fish oil, linseed oil, oiticica oil, soya oil, and tung oil, animal grease, castor oil, lard, palm kernel oil, peanut oil, perilla oil, safflower oil, tallow oil, walnut oil, and the like. Suitable examples of fatty acids alone or as components of oil include, but are not limited to, tallow acid, soya acid, myristic acid, linseed acid, crotonic acid, versatic acid, coconut acid, tall oil fatty acid, rosin acid, neodecanoic acid, neopentanoic acid, isostearic acid, 12-hydroxystearic acid, cottonseed acid, and the like.

The glycol or polyol is preferably selected from aliphatic, alicyclic, and aryl alkyl glycols. Suitable examples of glycols include, but are not limited to, ethylene glycol, propylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, pentaethylene glycol, hexaethylene glycol, heptaethylene glycol, octaethylene glycol, nonaethylene glycol, decaethylene glycol, 1,3-propanediol, 2,4-dimethyl-2-ethyl-hexane-1, 3-diol, 2,2-dimethyl-1, 2-propanediol, 2-ethyl-2-butyl-1, 3-propanediol, 2-ethyl-2-isobutyl- 1,3-propanediol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 2,2,4-tetramethyl-1,6-hexanediol, thiodiethanol, 1,2-cyclohexanedimethanol, 1,3-cyclohexanedimethanol,

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1,4-cyclohexanedimethanol, 2,2,4-trimethyl-1,3-pentanediol,
2,2,4-tetramethyl-1,3-cyclobutanediol, p-xylenediol, hydroxypivalyl
hydroxypivalate, 1,10-decanediol, hydrogenated bisphenol A,
trimethylolpropane, trimethylolethane, pentaerythritol, erythritol, threitol,
5 dipentaerythritol, sorbitol, glycerine, trimellitic anhydride, pyromellitic
dianhydride, dimethylolpropionic acid, and the like.

The polycarboxylic acid is preferably selected from the group
consisting of isophthalic acid, terephthalic acid, phthalic anhydride (acid),
adipic acid, tetrachlorophthalic anhydride, tetrahydrophthalic anhydride,
10 dodecanedioic acid, sebacic acid, azelaic acid, 1,4-cyclohexanedicarboxylic
acid, 1,3-cyclohexanedicarboxylic acid, maleic anhydride, fumaric acid,
succinic anhydride (acid), 2,6-naphthalenedicarboxylic acid, glutaric acid
and esters thereof.

The sulfonated waterborne alkyd resins useful in the invention
15 preferably have a K value, defined as the total number of moles (M_t) of each
reactant divided by the total equivalents of acid functionality (E_a), of about
1.0 to about 1.5, more preferably of about 1.0 to about 1.25, and an R
value, defined as the total equivalents of hydroxyl functionality (E_{OH}) divided
by the total equivalents of acid functionality (E_a), of about 1.0 to about 2.0,
20 more preferably of about 1.0 to about 1.5.

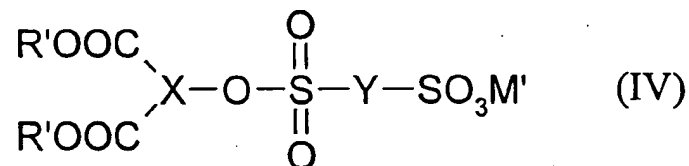
The K value is a measure of a resin's molecular weight that
increases as the K value decreases to 1.00. Since higher molecular weight
resins are better, K values that are closer to 1.00 are most preferred. The
R-value is proportional to the excess equivalents of hydroxyl functionality
25 used in the resin synthesis. An excess of hydroxyl functionality is preferred,
however this excess should not be so high as to render the resulting
coating water sensitive.

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The sulfomonomer of the sulfomonomer adduct is either a difunctional or a monofunctional monomer containing a $-\text{SO}_3\text{M}$ group attached to an aromatic nucleus where M is hydrogen or a metal ion such as, for example, Na^+ , Li^+ , K^+ , Ca^{2+} , Cu^{2+} , Fe^{2+} , or Fe^{3+} . The sulfomonomer as a difunctional monomer component may be a dicarboxylic acid (or a derivative thereof) containing a $-\text{SO}_3\text{M}$ group where M is as defined above. Suitable examples of the aromatic nucleus, to which the $-\text{SO}_3\text{M}$ group may be attached include, but are not limited to, benzene, naphthalene, anthracene, diphenyl, oxydiphenyl, sulfonyl-diphenyl, and methylenediphenyl.

Especially good results are obtained when the difunctional monomer is a sodium salt of a sulfoisophthalic acid, a sulfoterephthalic acid, a sulfophthalic acid, a 4-sulfo-naphthalene-2,7-dicarboxylic acid or a derivative thereof. More preferably, the difunctional monomer is 5-sodiosulfoisophthalic acid or a derivative such as dimethyl 5-sodiosulfoisophthalate. Other preferred difunctional monomers are lithium 5-sulfoisophthalic acid, dimethyl lithium 5-sulfoisophthalate, potassium 5-sulfoisophthalic acid, and dimethyl potassium 5-sulfoisophthalate.

Other effective difunctional monomers containing a $-\text{SO}_3\text{M}$ group attached to an aromatic nucleus include metal salts of aromatic sulfonic acids or their respective esters of the formula (IV):

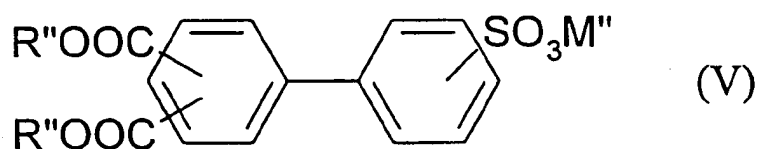


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wherein X is a trivalent aromatic hydrocarbon radical, Y is a divalent aromatic hydrocarbon radical, R' is hydrogen or an alkyl group of one to four carbon atoms, M' is hydrogen, Na⁺, Li⁺, or K⁺. Examples of preferred monomers of formula (IV) include, but are not limited to,

- 5 4-sodiosulfophenyl-3,5-dicarbomethoxybenzenesulfonate,
4-lithiosulfophenyl-3,5-dicarbomethoxybenzenesulfonate and
6-sodiosulfo-2-naphthyl-3,5-dicarbomethoxy-benzenesulfonate.

Still other effective difunctional monomers containing a -SO₃M group attached to an aromatic nucleus include metal salts of sulfodiphenyl ether
10 dicarboxylic acids or esters thereof of the formula (V):



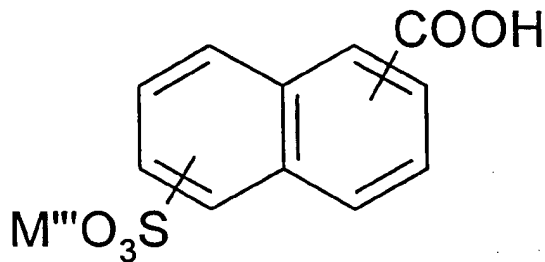
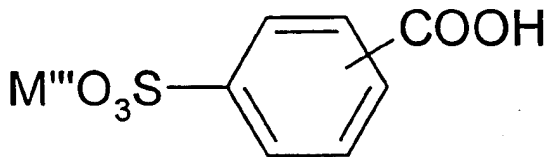
- wherein R'' is hydrogen, an alkyl group of one to eight carbon atoms, or
15 phenyl and M'' is hydrogen, K⁺, Na⁺, or Li⁺. Examples of preferred monomers include, but are not limited to, dimethyl
5-[4-(sodiosulfo)phenoxy]isophthalate, dimethyl 5-[4-(sodiosulfo)phenoxy]
terephthalate, and 5-[4-(sodiosulfo)phenoxy]isophthalic acid. Additional
examples of such monomers are disclosed in U.S. Pat. No. 3,734,874
20 incorporated herein by reference.

The type and amount of metal sulfonate selected for water dispersability can be varied to obtain useful ion-containing alkyd resins. As little as 2 mole percent based on total carboxylic acid content will impart a significant degree of water miscibility, however, at least 3 percent is
25 preferred. Water-soluble polyesters can be formulated with as much as 20 mole percent of the metal sulfonate. However, a practical upper limit based on the amount of branch-inducing intermediate required to counteract the water sensitivity effects is 9 percent, preferably 6 percent. Metal sulfonates

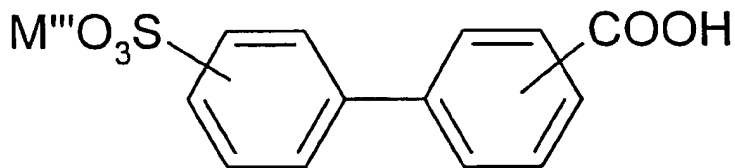
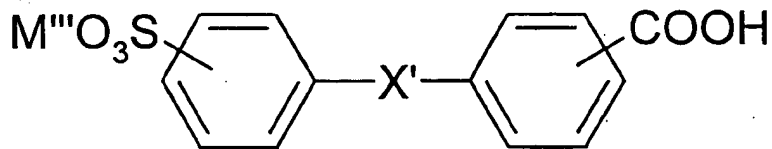
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that are most preferred include 5-sodiosulfoisophthalic acid, dimethyl 5-sodiosulfoisophthalate, lithium 5-sulfoisophthalic acid, dimethyl lithium 5-sulfoisophthalate, potassium 5-sulfoisophthalic acid, dimethyl potassium 5-sulfoisophthalate, 3-sodiosulfobenzoic acid and the like.

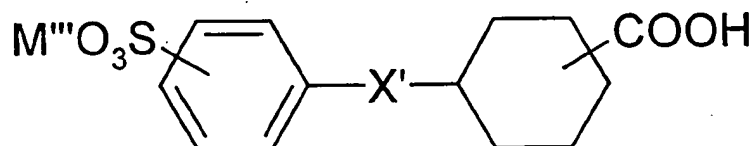
- 5 Optionally, the sulfomonomer containing at least one sulfonate group that may be reacted with a polyol to produce a polyol (e.g. a diol) sulfomonomer adduct may be a monofunctional sulfomonomer containing at least one sulfonate group that may be reacted with a polyol containing at least three hydroxyl groups. The monofunctional sulfomonomer is
- 10 preferably selected from the following group of sulfomonomers:



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where X is CH₂, SO₂, or O and M''' is an alkaline or alkaline earth metal.

When the polyol sulfomonomer adduct is prepared by reacting a
 5 difunctional sulfomonomer with a polyol, the polyol is preferably a diol.
 Suitable examples of diols include those described above with the following
 diols being more preferred: ethylene glycol, diethylene glycol,
 2,2,4-trimethyl-1, 3-pentanediol, 1,4-cyclohexanedimethanol,
 1,3-cyclohexane-dimethanol, hydroxypivalyl hydroxypivalate, dipropylene
 10 glycol, 1,6-hexanediol, 1,10-decanediol, 1,3-butanediol, hydrogenated
 bisphenol A, 1,4-butanediol and neopentyl glycol.

In addition to the amount of polyol reacted with the fatty acid, fatty
 ester or naturally occurring-partially saponified oil according to the preferred
 step, and in addition to the polyol used in the preparation of the
 15 sulfomonomer adduct from a monofunctional sulfomonomer, an additional
 amount of a polyol or other branching agent such as a polycarboxylic acid
 may be used to increase the molecular weight and branching of the
 waterborne alkyd resin. These branching agents are preferably selected
 from trimethylolethane, pentaerythritol, erythritol, threitol, dipentaerythritol,
 20 sorbitol, glycerine, trimellitic anhydride, pyromellitic dianhydride,
 dimethylolpropionic acid, and trimethylolpropane.

In order for the alkyd resin to serve as a reactive filming aid (via
 oxidative coupling) in a hybrid latex and become incorporated into the
 crosslinked polymer film, it is preferred that the alkyd have some finite oil
 25 length - long, medium or short. The finite oil length or oil content is
 generally between about 20 wt% and about 90 wt% in the alkyd
 composition based on the total weight of the alkyd resin. A "long" oil alkyd
 has an oil length or oil content of about 60-90 wt% based on the total weight

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of the alkyd resin. A "medium" oil alkyd has oil content of about 40-60 wt% based on the total weight of the alkyd resin. A "short" oil alkyd has an oil length or oil content of about 20-40 wt% based on the total weight of the alkyd resin.

5 Ethylenically Unsaturated Monomer

The acrylic portion of the acrylic-modified waterborne alkyd resin may be prepared by free radical polymerization of at least one ethylenically unsaturated monomer in the presence of a sulfonated waterborne alkyd as described above. Examples of suitable ethylenically unsaturated monomers include, but are not limited to, styrenic monomers such as styrene, α -methyl styrene, vinyl naphthalene, vinyl toluene, chloromethyl styrene and the like; ethylenically unsaturated species such as, for example, methyl acrylate, acrylic acid, methacrylic acid, methyl methacrylate, ethyl acrylate, ethyl methacrylate, butyl acrylate, butyl methacrylate, isobutyl acrylate, isobutyl methacrylate, ethylhexyl acrylate, ethylhexyl methacrylate, octyl acrylate, octyl methacrylate, glycidyl methacrylate, carbodiimide methacrylate, alkyl crotonates, vinyl acetate, di-n-butyl maleate, di-octylmaleate, and the like; and nitrogen containing monomers including t-butylaminoethyl methacrylate, dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate, N,N-dimethylaminopropyl methacrylamide, 2-t-butylaminoethyl methacrylate, N,N-dimethylaminoethyl acrylate, N-(2-methacryloyloxy-ethyl)ethylene urea, and methacrylamidoethylethylene urea, and mixtures thereof. Other examples of suitable ethylenically unsaturated monomers include, but are not limited to, ethylenically unsaturated monomers having at least one latent oxidative functionality (LOF).

The LOF group may be any pendant moiety, which is capable of (i) surviving the polymerization process and (ii) participating in or promoting oxidative crosslinking of the modified alkyd. After polymerization of the acrylic monomer, a modified alkyd of the invention possesses sufficient

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LOF groups to increase or amplify the degree of crosslinking normally found in acrylic modified waterborne alkyd resins that contain no LOF groups. In other words, sufficient LOF groups remain to increase or enhance the effective crosslinking of the hybrid resin.

5 The presence of a LOF group on the modified alkyd aids in crosslinking upon or after film formation. With a modified alkyd of the invention, crosslinking may occur between LOF groups of acrylic monomer(s), between a LOF group of an acrylic monomer and a ethylenically unsaturated functionality of the alkyd, or between ethylenically
10 unsaturated functionalities of the alkyd. Capable of undergoing an oxidative reaction, the LOF group participates in or promotes oxidative crosslinking as a source of free radicals to generate a free-radical flux. Preferably the LOF group is an ethylenic unsaturation such as, but not limited to, allyl and vinyl groups. The LOF group may also preferably be an acetoacetyl moiety
15 or enamine moiety. Preparation of enamines from acetoacetyl groups is described in U.S. Patents 5,296,530, 5,494,975, and 5,525,662, all incorporated herein by reference. While addition of LOF enhances crosslinking, the embodiment of this invention is not limited to its use for producing ink films having alkali resistance.

20 Examples of acrylic monomers having latent oxidatively-functional (LOF) groups include, but are not limited to, allyl methacrylate, vinyl methacrylate, acetoacetoxyethyl methacrylate, hydroxybutenyl methacrylate, the allyl or diallyl ester of maleic acid, poly(allyl glycidyl ether) and the like, and mixtures thereof.

25 Water-based Hybrid Alkyd-Acrylic Latexes

 The water-based latexes of the invention may be prepared by the polymerizing at least one ethylenically unsaturated monomer in the presence of an aqueous dispersion of a waterborne alkyd having at least one pendant sulfonate functionality. The water-based latexes of the
30 invention are stable at the same pHs (pH > 7) as latexes prepared from

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traditional waterborne alkyds. However, unlike hybrid latexes of traditional waterborne alkyds, the sulfonated waterborne alkyd based hybrid latexes of the invention are also stable at pH 7, even as low as pH 4.0-4.5. In the water-based latexes of the invention, the modified alkyd generally exists as particles in water. As discussed above, if monomers that contain LOF groups are included in the acrylic portion of the hybrid resin, sufficient LOF groups should remain after the polymerization process to enhance oxidative crosslinking of films formed from the resulting water-based alkyd latex. Since the LOF group functions to increase the effective crosslinking of the alkyd, post-polymerization survival of sufficient LOF groups not only allows for their co-reactivity with other LOF groups and/or waterborne alkyd functionality upon or after film formation but may also promote similar oxidative crosslinking between waterborne alkyd functionalities. As a result of such co-reactivity between LOF groups and/or alkyd functionalities, film properties such as, for example, solvent resistance and hardness can be improved.

As discussed above, the ethylenically unsaturated monomer may be added either as a mixture of at least one ethylenically unsaturated monomer or as a mixture of at least one ethylenically unsaturated monomer and an LOF acrylic comonomer. Addition of an ethylenically unsaturated monomer may be conducted in a one-stage or multiple-stage (e.g. core-shell) process. Preferably, the ethylenically unsaturated monomer is added in a one-stage process. In cases where a LOF acrylic monomer is desired, addition of the LOF acrylic monomer or monomers in a one-stage process results in a homogeneous acrylic polymer (*i.e.*, simple terpolymer) which contains a sufficient number of LOF groups (e.g. allyl, vinyl) capable of reacting with other LOF groups or alkyd functionality upon or after film formation or promoting reaction between functionalities on the alkyd.

Addition of the LOF acrylic monomer in a multiple-stage process produces a heterogeneous acrylic polymer. For example, in a two-stage

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process, the first stage of the addition may produce a core polymer of preferably an acrylic or styrene/acrylic polymer that is often pre-crosslinked with a multi-functional monomer such as trimethylolpropane triacrylate. The second stage of the addition produces a shell polymer of preferably a
5 styrene/acrylic polymer that contains a high level of LOF groups, such as reactive allyl and/or vinyl moieties. Monomers for use in such one- or multiple-stage polymerization processes are described in U.S. Patent 5,539,073, incorporated herein by reference. The LOF groups may be located at both the termini of the polymer as well as along the polymer
10 backbone.

As discussed above, preferably the water-based latex of the invention is prepared under emulsion polymerization conditions. In general, during emulsion polymerization of the LOF acrylic polymer compositions, it is primarily the ethylenic unsaturation moiety of the acrylic that undergoes
15 polymerization and not the LOF group. If the LOF group participates in the polymerization, polymerization conditions are such that enough LOF groups survive in order to oxidatively crosslink with other LOF groups and/or waterborne alkyd functionality and/or to enhance oxidative crosslinking between waterborne alkyd functionalities upon or after film formation.
20 Survival of LOF groups, such as allyl or vinyl moieties, upon polymerization can be achieved by manipulating the differences in reactivity of the ethylenically unsaturated groups. For example, the ethylenically unsaturated acrylic moiety of an allyl or vinyl functionalized acrylic monomer has greater reactivity upon polymerization with styrenic monomers than the
25 LOF allyl or vinyl moiety. As a result, the final polymer contains LOF groups. A description of manipulation of allyl functionalized acrylic polymer compositions to promote survival of the allyl moiety upon emulsion polymerization may be found in U.S. Patent 5,539,073, incorporated herein by reference. Vinyl functionalized acrylic polymer compositions may be

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manipulated in a manner similar to that applied to allyl functionalized acrylic polymer compositions.

When the LOF group of the acrylic polymer is an acetoacetoxy moiety, under emulsion polymerization conditions it is the ethylenically unsaturated moiety that polymerizes. The acetoacetoxy moiety is unaffected by, and thus survives, the polymerization process.

It is not required that the components of the polymerization undergo extensive shearing in order to produce a stable mixture prior to the polymerization. In addition, any residual solvent present in the alkyl component aids in producing latexes of good quality.

The polymerization process by which the hybrid latexes are made may also include components including, but not limited to, initiators, reducing agents, or catalysts. Suitable initiators include conventional initiators such as ammonium persulfate, ammonium carbonate, hydrogen peroxide, t-butylhydroperoxide, ammonium or alkali sulfate, di-benzoyl peroxide, lauryl peroxide, di-tertiarybutylperoxide, 2, 2'-azobisisobuteronitrile, benzoyl peroxide, and the like.

Suitable reducing agents are those which increase the rate of polymerization and include, for example, sodium bisulfite, sodium hydrosulfite, sodium formaldehyde sulfoxylate, ascorbic acid, isoascorbic acid, and mixtures thereof.

Suitable catalysts are those compounds that promote decomposition of the polymerization initiator under the polymerization reaction conditions thereby increasing the rate of polymerization. Suitable catalysts include transition metal compounds and driers. Examples of such catalysts include, but are not limited to, ferrous sulfate heptahydrate, ferrous chloride, cupric sulfate, cupric chloride, cobalt acetate, cobaltous sulfate, and mixtures thereof.

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Optionally, a conventional surfactant or a combination of surfactants may be used as a costabilizer or cosurfactant, such as an anionic or non-ionic emulsifier, in the suspension or emulsion polymerization preparation of a hybrid latex of the invention. Examples of preferred surfactants include, but are not limited to, alkali or ammonium alkylsulfate, alkylsulfonic acid, or fatty acid, oxyethylated alkylphenol, or any combination of anionic or non-ionic surfactant. A more preferred surfactant monomer is HITENOL HS-20 (which is a polyoxyethylene alkylphenyl ether ammonium sulfate available from DKS International, Inc. of Japan). A list of suitable surfactants is available in the treatise: McCutcheon's Emulsifiers & Detergents, North American Edition and International Edition, MC Publishing Co., Glen Rock, NJ, 1993. Preferably a conventional surfactant or combination of surfactants may be added when the alkyd portion of the hybrid resin is present in an amount up to about 35 wt%, generally about 5-30 wt% of the total solids of the latex.

If the resulting hybrid latex is formulated with drier salts typically used in alkyd coatings and LOF moieties are present in the acrylic portion of the hybrid, significant improvements in, among other properties, hardness and solvent resistances is observed. While the alkyd-acrylic hybrid provides good alkali resistance, the presence of the LOF acrylic portion of the hybrid may also improve certain physical and mechanical film properties. The improved properties are typically those related to higher crosslink density than that observed for hybrid resins containing non-LOF acrylics.

In general, the alkyd portion of the hybrid latex may represent about 5-60 wt%, preferably about 10-50 wt%, more preferably about 20-40 wt% of the total solids of the latex; while the acrylic portion of the hybrid latex may represent about 40-95wt %, preferably about 50-90 wt%, more preferably about 60-80 wt% of the total solids of the latex. Such hybrid latexes are suitable for use in ink formulations.

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An ink formulation of the present invention contains a hybrid alkyd-acrylic latex of the present invention and at least one additive, and may be prepared by techniques known in the art, e.g. as disclosed in "Design and Formulation of Water Based Inks", pp. 220-254 and "Typical Starting Formulations for Water Based Inks", pp. 311-332, *Chemistry and Technology of Water Based Inks*, P. Laden, (Chapman and Hall, London, U.K.). Examples of suitable ink formulations prepared from the ink formulations of the present invention include, for example, flexographic inks, rotogravure inks, screen printing inks, ink jet inks, packaging inks, primers, and overprints. Ink formulations of the invention contain significantly less solvent, having less than about 25 wt% to as low as about 1 wt% VOC content. The waterborne alkyd portion of the hybrid resin retains the desirable properties of an alkyd while the acrylic portion of the resin improves the hardness and durability of the hybrid alkyd resin. When an LOF acrylic monomer is used, the LOF portion of the acrylic resin compliments or enhances the oxidative crosslinking ability of the hybrid alkyd resin at ambient temperature. The coating compositions of the invention produce coatings that have high gloss, fast cure, and good alkali resistance.

A typical ink formulation of the present invention using the hybrid alkyd-acrylic resin, may contain one or more other components as is known in the art. Suitable additives include, but are not limited to, driers, drier activators, waxes, rheology and flow control agents, extenders, reactive coalescing aids, plasticizers, flattening agents, pigment wetting and dispersing agents and surfactants, ultraviolet absorbers, ultraviolet light stabilizers, tinting pigments, colorants, dyes, defoaming and antifoaming agents, anti-settling, anti-sag and bodying agents, anti-skinning agents, anti-flooding and anti-floating agents, biocides, thickening agents, coalescing agents, and co-solvents.

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Examples of such additives include, but are not limited to, one or more leveling, rheology, and flow control agents such as silicones, fluorocarbons or cellulose; extenders; reactive coalescing aids such as those described in U.S. Pat. No. 5,349,026, incorporated herein by reference; plasticizers; flattening agents; pigment wetting and dispersing agents and surfactants; ultraviolet (UV) absorbers; UV light stabilizers; tinting pigments; colorants; dyes; pigment dispersions; defoaming and antifoaming agents; anti-settling, anti-sag and bodying agents; anti-skinning agents; anti-flooding and anti-floating agents; biocides, corrosion inhibitors; thickening agents; coalescing agents; waxes; fillers; co-resins; and buffers. Specific examples of such additives can be found in Raw Materials Index, published by the National Paint & Coatings Association, 1500 Rhode Island Avenue, N.W., Washington, D.C. 20005. Further examples of such additives and emulsion polymerization methodology may be found in U.S. Pat. No. 5,371,148, incorporated herein by reference.

Examples of flattening agents include, but are not limited to, synthetic silica, available from the Davison Chemical Division of W. R. Grace & Company under the SYLOID® tradename; polypropylene, available from Hercules Inc. under the HERCOFLAT® tradename; and synthetic silicate, available from J. M. Huber Corporation under the ZEOLEX® tradename.

Examples of dispersing agents and surfactants include, but are not limited to, sodium bis(tridecyl) sulfosuccinnate, di(2-ethylhexyl) sodium sulfosuccinnate, sodium dihexylsulfosuccinnate, sodium dicyclohexyl sulfosuccinnate, diamyl sodium sulfosuccinnate, sodium diisobutyl sulfosuccinnate, disodium iso-decyl sulfosuccinnate, disodium ethoxylated alcohol half ester of sulfosuccinnic acid, disodium alkyl amido polyethoxy sulfosuccinnate, tetra-sodium N-(1,2-dicarboxyethyl)-N-octadecyl sulfosuccinamate, disodium N-octasulfosuccinamate, sulfated ethoxylated nonylphenol, 2-amino-2-methyl-1-propanol, and the like.

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Examples of viscosity, suspension, and flow control agents include, but are not limited to, polyaminoamide phosphate, high molecular weight carboxylic acid salts of polyamine amides, and alkylene amine salts of an unsaturated fatty acid, all available from BYK Chemie U.S.A. under the
5 ANTI TERRA ® tradename. Further examples include polysiloxane copolymers, polyacrylate solution, cellulose esters, hydroxyethyl cellulose, hydrophobically-modified hydroxyethyl cellulose, hydroxypropyl cellulose, polyamide wax, polyolefin wax, carboxymethyl cellulose, ammonium polyacrylate, sodium polyacrylate, hydroxypropyl methyl cellulose, ethyl
10 hydroxyethyl cellulose, polyethylene oxide, guar gum and the like. Other examples of thickeners include the methylene/ethylene oxide associative thickeners and water soluble carboxylated thickeners such as, for example, UCAR POLYPHOBE ® by Union Carbide.

Several proprietary antifoaming agents are commercially available
15 and include, for example, BUBREAK ® of Buckman Laboratories Inc., BYK ® of BYK Chemie, U.S.A., FOAMASTER ® and NOPCO ® of Henkel Corp./Coating Chemicals, DREWPLUS ® of the Drew Industrial Division of Ashland Chemical Company, TRYSOL ® and TROYKYD ® of Troy Chemical Corporation, and SAG ® of Union Carbide Corporation.

20 Examples of biocides include, but are not limited to, 4,4-dimethyloxazolidine, 3,4,4-trimethyloxazolidine, modified barium metaborate, potassium N-hydroxy-methyl- N-methyldithiocarbamate, 2-(thiocyano-methylthio) benzothiazole, potassium dimethyl dithiocarbamate, adamantane, N-(trichloromethylthio)phthalimide,
25 2,4,5,6-tetrachloro-isophthalonitrile, orthophenyl phenol, 2,4,5-trichlorophenol, dehydroacetic acid, copper naphthenate, copper octoate, organic arsenic, tributyl tin oxide, zinc naphthenate, and copper 8-quinolinate.

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Examples of U.V. absorbers and U.V. light stabilizers include among others substituted benzophenone, substituted benzotriazoles, hindered amines, and hindered benzoates, available from American Cyanamid Company under the CYASORB UV ® tradename, and
5 diethyl-3-acetyl-4-hydroxy-benzyl-phosphonate, 4-dodecyloxy-2-hydroxy benzophenone, and resorcinol monobenzoate.

Examples of solvents and coalescing agents are well known and include but are not limited to ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, isobutanol, ethylene glycol monobutyl ether, propylene glycol
10 n-butyl ether, propylene glycol methyl ether, propylene glycol monopropyl ether, dipropylene glycol methyl ether, diethylene glycol monobutyl ether, trimethylpentanediol mono-isobutyrate, ethylene glycol mono-octyl ether, diacetone alcohol, TEXANOL ® ester alcohol (Eastman Chemical Company), and the like. Such solvents and coalescing aids may also
15 include reactive solvents and coalescing aids such as diallyl phthalate, SANTOLINK XI-100 ® polyglycidyl allyl ether from Monsanto, and others as described in U.S. Pat. Nos. 5,349,026 and 5,371,148, incorporated herein by reference.

Pigments suitable for use in the ink formulations envisioned by the
20 invention are the typical organic and inorganic pigments, well-known to one of ordinary skill in the art of surface coatings, especially those set forth by the Colour Index, 3d Ed., 2d Rev., 1982, published by the Society of Dyers and Colourists in association with the American Association of Textile Chemists and Colorists. Examples include, but are not limited to, the
25 following: titanium dioxide, barytes, clay, or calcium carbonate, CI Pigment White 6 (titanium dioxide); CI Pigment Red 101 (red iron oxide); CI Pigment Yellow 42; CI Pigment Blue 15, 15:1, 15:2, 15:3, 15:4 (copper phthalocyanines); CI Pigment Red 49:1; and CI Pigment Red 57:1.

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Colorants such as phthalocyanine blue, molybdate orange, or carbon black are also suitable for the coating compositions of the invention. Commercial pigment dispersions comprising these pigments may also be used.

5 The ink formulation or overprint may be applied to a substrate using any of the standard printing methods for aqueous inks such as flexography or rotogravure. The substrate can be any common substrate such as paper, polyethylene film, polyester film, polypropylene films, metallic and metallized film, polyethylene coated board and the like. The ink formulations of the present invention are especially suited for good
10 conveyor line lube resistance when printing polyethylene coated board. The ink formulation of the invention may be cured at room temperature (ambient cure), at elevated temperatures (thermal cure), or photochemically cured.

15 This invention can be further illustrated by the following examples of preferred embodiments thereof, although it will be understood that these examples are included merely for purposes of illustration and are not intended to limit the scope of the invention unless otherwise specifically indicated.

EXAMPLES

20 The examples of various ink formulations of the invention use the following materials not described above:

ACTIV 8 accelerator sold by R.T. Vanderbilt, Inc., Norwalk, CT

COBALT HYDROCURE II drier, ZIRCONIUM HYDROCEM drier,
and DRI-RX-HF accelerator sold by OMG, Cleveland, Ohio

25 EKTASOLVE EB coalescent (co-solvent) sold by Eastman Chemical Company, Kingsport, Tennessee

FASCAT 4100 an esterification catalyst, sold by M&T Chemicals, Rahway, New Jersey

30 PAMOLYN 200 a tall oil fatty acid, sold by Hercules Incorporated, Wilmington, Delaware

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SUNSPERSE 6000 BLUE 15:3 PIGMENT DISPERSION sold by Sun Chemical Corp., Paterson, N.J.

FLEXONIC 600 wax, sold by Lawter, International, Kenosha, Wisconsin.

- 5 The following methods were used to evaluate the inks prepared according to the invention:

Alkali Resistance Testing

- 10 A portion of the prepared ink is placed on a polyethylene coated paper stock (milk carton) and is drawn into an ink film using a #3 RD rod on an RK Printcoater. The resultant coated stock was placed facing the airflow in a 100° C. oven for fifteen seconds. The printed board was then air dried at ambient temperatures overnight. To assess the alkaline resistance of the printed ink, five drops of a 3% KLENSADE Sani-glide solution were placed on the printed board. After exposure periods of 5, 15, 30, 60, and 90
- 15 minutes, the line lube solution was removed by wiping four strokes in one direction with a paper tissue. The area where the lubricant spot was located is then visually evaluated for ink removal. The visual evaluation is given a rating of 0 to 10 with 0 being total removal and 10 being no removal. The test result of inks prepared from Example latexes 2 through
- 20 17, having been printed on the polyethylene coated stock, are shown in Table 2. An epoxy ester control ink is included for comparison purposes.

Gloss Measurement

- 25 Gloss was measured on the printed ink films by averaging three 60° gloss readings taken in different locations using a Byk Gardner Micro Gloss gloss meter. The results are shown in Table 3.

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EXAMPLESExample 1: Preparation and Dispersion of Water-Dispersible Sulfonated Alkyd Resin

- 5 Step 1: An adduct of neopentyl glycol (NPG) and 5-sodiosulfoisophthalic acid (SIP) was first prepared by reacting NPG (2483.5g, 23.88 mol); SIP (93.3%) (1608.5g, 5.6 mol); distilled water (276.0g); and the catalyst, FASCAT 4100 (3.3g) in a three-neck, round bottom flask equipped with a mechanical stirrer, a steam-jacketed partial
10 condenser, a Dean-Stark trap, a nitrogen inlet, and a water condenser. The reaction temperature was gradually increased from 130 C to 190 C in a period of five hours and the condensate (water) collected in a Dean-Stark trap. The reaction was allowed to continue until an acid number of 3 was obtained. A portion of the resultant product was used in the following step.
- 15 Step 2: Into a three-neck, round-bottom flask (3L) equipped with the same configuration as above were charged the NPG/SIP adduct (497.0g); phthalic anhydride (PA) (357.4g, 2.42 mol); pentaerythritol (PE) (233.8g, 1.72 mol); PAMOLYN 200 (tall oil fatty acid) (985.9g, 3.40 mol); and FASCAT 4100 (1.54g). The reaction temperature was gradually increased
20 to 230 C in one hour. The reaction was allowed to continue for about three more hours until an acid number of 8 was obtained. The resulting resin was allowed to cool and subsequently isolated.

Preparation of Aqueous Dispersion: The viscous resin from Step 2 was warmed to 80°C in an oven and subsequently charged (100g) into a
25 flask equipped with a water condenser. The resin was heated to 120°C and stirred under a nitrogen atmosphere. The resulting resin melt was allowed to cool to 80°C and distilled water (100g) was added dropwise. During the dispersing process, the temperature was further reduced to 50°C when a homogeneous resin solution was obtained. The stirring was allowed to
30 continue and additional water (22g) added to give an aqueous resin with 45% solids.

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Examples 2- 6: Preparation of Latexes by Emulsion Polymerization of Alkyd / LOF Acrylic Hybrid Resins

5 To a 1000mL resin kettle equipped with a condenser, nitrogen purge, and an above surface feed tube were added water and the alkyd dispersion from Example 1. A nitrogen purge was begun, then the contents of the reactor brought up to 40°C, an initiator charge composed of 0.35g of ammonium persulfate dissolved in 6.0g of water, 0.35g of sodium bisulfite
10 dissolved in 6.0g of water, and 2.32g of a 1% ammonium iron sulfate solution in water were added to the reactor. The acrylic monomer composition feed, along with any chain transfer agent, was then begun and fed over approximately 255 minutes. Simultaneously, initiator feeds composed of 2.49g of tert-butyl hydroperoxide (70%) dissolved in 45.0g of
15 water and 1.23g of d-isoascorbic acid and 0.58g of ammonium bicarbonate dissolved in 45.0g of water was begun and fed at 0.18g/min. After the monomer feed was completed, the reaction was held for 15 minutes at 40°C with continued addition of the initiator solution. After all the feeds were completed, additional initiator feeds of 5.25g of tert-butyl
20 hydroperoxide (70%) dissolved in 21.0g of water and 2.56g of d-isoascorbic acid and 2.32g of ammonium hydroxide (28%) dissolved in 42.0g of water were fed into the reaction vessel over a 60 minute period. After the initiator feeds had finished, the emulsion was cooled, filtered through a 100-mesh wire screen, and filterable solids or scrap collected. The particle size,
25 viscosity and pH of the resulting alkyd-acrylic hybrid resin latexes were determined and summarized in Table 1.

Example 7 - 14: Preparation of Latexes by Emulsion Polymerization of Alkyd / non-LOF Acrylic Hybrid Resins

30

To a 1000mL resin kettle equipped with a condenser, nitrogen purge, and an above surface feed tube were added water and the alkyd dispersion from Example 1. A nitrogen purge was begun, then the contents of the

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reactor brought up to 40°C, an initiator charge composed of 0.41g of ammonium persulfate dissolved in 6.0g of water, 0.41g of sodium bisulfite dissolved in 6.0g of water, and 2.71g of a 1% ammonium iron sulfate solution in water were added to the reactor. The acrylic monomer composition feed, along with any chain transfer agent, was then begun and fed over approximately 255 minutes. Simultaneously, initiator feeds composed of 2.90g of tert-butyl hydroperoxide (70%) dissolved in 45.0g of water and 1.44g of d-isoascorbic acid and 0.68g of ammonium bicarbonate dissolved in 45.0g of water was begun and fed at 0.18g/min. After the monomer feed was completed, the reaction was held for 15 minutes at 40°C with continued addition of the initiator solution. After all the feeds were completed, additional initiator feeds of 6.12g of tert-butyl hydroperoxide (70%) dissolved in 21.0g of water and 2.98g of d-isoascorbic acid and 2.71g of ammonium hydroxide (28%) dissolved in 42.0g of water were fed into the reaction vessel over a 90 minute period. After the initiator feeds had finished, the emulsion was cooled, filtered through a 100-mesh wire screen, and filterable solids or scrap collected. The particle size, viscosity and pH of the resulting alkyd-acrylic hybrid resin latexes were determined and summarized in Table 1.

Example 15: Preparation of Latex by Emulsion Polymerization of Alkyd / non-LOF Acrylic Hybrid Resins

To a 1000mL resin kettle equipped with a condenser, nitrogen purge, and an surface feed tube were added water, the alkyd dispersion from Example 1 (Table 1) and 10.07g of Trem LF-40 reactive surfactant. A nitrogen purge was begun, then the contents of the reactor brought up to 40°C, an initiator charge composed of 0.40g of ammonium persulfate dissolved in 6.0g of water, 0.40g of sodium bisulfite dissolved in 6.0g of water, and 2.68g of a 1% ammonium iron sulfate solution in water were added to the reactor. The acrylic monomer composition feed was then begun and fed over approximately 255 minutes. Simultaneously, initiator

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feeds composed of 2.88g of tert-butyl hydroperoxide (70%) dissolved in 45.0g of water and 1.42g of d-isoascorbic acid and 0.67g of ammonium bicarbonate dissolved in 45.0g of water was begun and fed at 0.18g/min. After the monomer feed was completed, the reaction was held for 15 minutes at 40°C with continued addition of the initiator solution. After all the feeds were completed, additional initiator feeds of 6.06g of tert-butyl hydroperoxide (70%) dissolved in 21.0g of water and 2.95g of d-isoascorbic acid and 2.68g of ammonium hydroxide (28%) dissolved in 42.0g of water were fed into the reaction vessel over a 90 minute period. After the initiator feeds had finished, the emulsion was cooled, filtered through a 100-mesh wire screen, and filterable solids or scrap collected. The particle size, viscosity and pH of the resulting alkyd-acrylic hybrid resin latexes were determined and summarized in Table 1.

15 Example 16: Preparation of Latex by Emulsion Polymerization of Alkyd / non-LOF Acrylic Hybrid Resins

To a 1000mL resin kettle equipped with a condenser, nitrogen purge, and an above surface feed tube were added water, the alkyd dispersion from Example 1 and 4.15g of Hitenol HS-10 reactive surfactant. A nitrogen purge was begun, then the contents of the reactor brought up to 40°C, an initiator charge composed of 0.40g of ammonium persulfate dissolved in 6.0g of water, 0.40g of sodium bisulfite dissolved in 6.0g of water, and 2.68g of a 1% ammonium iron sulfate solution in water were added to the reactor. The acrylic monomer composition feed was then begun and fed over approximately 255 minutes. Simultaneously, initiator feeds composed of 2.88g of tert-butyl hydroperoxide (70%) dissolved in 45.0g of water and 1.42g of d-isoascorbic acid and 0.67g of ammonium bicarbonate dissolved in 45.0g of water was begun and fed at 0.18g/min. After the monomer feed was completed, the reaction was held for 15 minutes at 40°C with continued addition of the initiator solution. After all the feeds were completed, additional initiator feeds of 6.06g of tert-butyl hydroperoxide

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(70%) dissolved in 21.0g of water and 2.95g of d-isoascorbic acid and 2.68g of ammonium hydroxide (28%) dissolved in 42.0g of water were fed into the reaction vessel over a 90 minute period. After the initiator feeds had finished, the emulsion was cooled, filtered through a 100-mesh wire screen, and filterable solids or scrap collected. The particle size, viscosity and pH of the resulting alkyd-acrylic hybrid resin latexes were determined and summarized in Table 1.

10 Example 17: Preparation of Latexes by Emulsion Polymerization of Acrylic Resins – Control

To a 1000mL resin kettle equipped with a condenser, nitrogen purge, and an above surface feed tube were added water and 9.92g of the reactive surfactant, Hitenol HS-20 (19.5% solution in water) (Table 1). A nitrogen purge was begun, then the contents of the reactor brought up to 80°C, and an initiator charge composed of 0.86g of ammonium persulfate in 6.0g of water was added to the reactor. The acrylic monomer composition feed was then begun and fed over approximately 150 minutes. Simultaneously, initiator feed composed of 0.86g of ammonium persulfate, 0.95g of ammonium carbonate and 19.55g of Hitenol HS-20 (19.5% solution in water) dissolved in 45.0g of water was begun and fed at 0.44g/min. After the monomer feed was completed, the reaction was held for 15 minutes at 80°C with continued addition of the initiator solution. After all the feeds were completed, a 3.81g charge of 1% ammonium iron sulfate was added to the reaction vessel. Simultaneously, additional initiator feeds of 5.72g of tert-butyl hydroperoxide (70%) dissolved in 21.0g of water and 2.78g of d-isoascorbic acid and 3.81g of ammonium hydroxide (28%) dissolved in 21.0g of water were fed into the reaction vessel over a 60 minute period. After the initiator feeds had finished, the emulsion was cooled, filtered through a 100 mesh wire screen, and filterable solids or scrap collected. The particle size, viscosity and pH of the resulting acrylic resin latexes were determined and summarized in Table 1.

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Examples 18 - 33: Preparation and Testing of Alkali Resistant Ink Films

Using a typical laboratory stirrer, a drier package additive was prepared by placing 47.4 parts of EKTASOLVE EB into a mixing vessel. While stirring, 5.6 parts of isopropyl alcohol was slowly added. This was followed in order by the addition of 13.9 parts of OMG 5% COBALT HYDROCURE II, 27.5 parts of OMG 12% ZIRCONIUM HYDROCEM, and 5.6 parts of ACTIV8 while maintaining agitation. After the drier package was blended, a simple ink formulation was prepared by placing 51.5 parts of the hybrid alkyd-acrylic latexes from Examples 2 - 17 into a mixing vessel and placing under agitation. A pH adjustment was made by first blending 0.3 parts of 2,2 dimethylethanolamine with 3.6 parts of water. This buffer was then added to the latex while stirring. 2.8 parts of FLEXONIC 600 wax was added to the mixture. This was followed by slowly adding 39.6 parts of SUNSPERSE 6000 BLUE 15:3 DISPERSION. The formulation was completed by very slowly adding 2.2 parts of the drier package previously prepared. The total blend was allowed to mix for thirty minutes.

Comparative Example 1: Ink Film Based on Epoxy Ester Latex

The control ink used in this experiment was an industry standard epoxy ester ink prepared with EPOTUFF E-92-737 resin, a commercially available ink resin from Reichold, used for printing on milk cartons and designed to have good alkali resistance.

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Table 2: Alkali Resistance Testing

Latex Ex.	Ink Ex.	5 min.	15 min.	30 min.	60 min.	90 min.
Control	Control	10.0	10.0	4.0	0.0	0.0
2	18	10.0	10.0	8.5	2.0	3.0
3	19	9.5	8.0	2.0	0.0	0.0
4	20	2.0	0.0	0.0	0.0	0.0
5	21	10.0	9.9	9.9	9.5	6.0
6	22	9.8	9.9	9.8	9.7	9.5
7	23	10.0	10.0	10.0	8.0	9.8
8	24	9.0	2.0	8.0	3.0	5.0
9	25	1.0	0.0	1.0	0.0	0.0
10	26	10.0	9.9	9.9	9.8	9.0
11	27	10.0	10.0	9.9	9.9	8.5
12	28	9.8	9.9	10.0	8.5	9.0
13	29	10.0	9.8	10.0	9.0	5.0
14	30	0.0	0.0	0.0	0.0	0.0
15	31	10.0	10.0	10.0	9.0	10.0
16	32	10.0	10.0	9.9	9.8	10.0
17	33	9.9	9.0	9.0	0.0	0.0

Scale rankings are from 0 to 10, where 0 is complete removal of ink and 10 in no change.

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Table 3: Gloss Measurements

60° gloss

Latex example	Ink example	Gloss (Avg. 3 readings)
Control	Control	30.4
2	18	48.2
3	19	45.3
4	20	44.8
5	21	44.6
6	22	48.4
7	23	50.2
8	24	47.1
9	25	45.4
10	26	44.6
11	27	44.0
12	28	47.2
13	29	46.3
14	30	42.3
15	31	44.8
16	32	42.4
17	33	10.2

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

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CLAIMS

What is Claimed is:

1. A water-based hybrid alkyd-acrylic latex comprising at least one
5 ethylenically unsaturated monomer polymerized in the presence of a
waterborne alkyd having at least one pendant sulfonate functionality.
2. The water based hybrid alkyd-acrylic latex of claim 1 wherein the
ethylenically unsaturated monomer is selected from the group consisting of
styrene, α -methyl styrene, vinyl naphthalene, vinyl toluene, chloromethyl
10 styrene, methyl acrylate, acrylic acid, methacrylic acid, methyl methacrylate,
ethyl acrylate, ethyl methacrylate, butyl acrylate, butyl methacrylate,
isobutyl acrylate, isobutyl methacrylate, ethylhexyl acrylate, ethylhexyl
methacrylate, octyl acrylate, octyl methacrylate, glycidyl methacrylate,
carbodiimide methacrylate, alkyl crotonates, vinyl acetate, di-n-butyl
15 maleate, di-octylmaleate, t-butylaminoethyl methacrylate, dimethylamino-
ethyl methacrylate, diethylaminoethyl methacrylate, N,N-dimethylamino-
propyl methacrylamide, 2-t-butylaminoethyl methacrylate, N,N-dimethyl-
aminoethyl acrylate, N-(2-methacryloyloxy-ethyl)ethylene urea, and
methacrylamidoethylethylene urea, and mixtures thereof.
- 20 3. The water based hybrid alkyd-acrylic latex of claim 1 wherein the
alkyd portion is present from 5 to 60 wt.% and the acrylic portion is present
from 40 to 95 wt. %.
4. The water based hybrid alkyd-acrylic latex-of claim 1 wherein the
alkyd portion is present from 10-50 wt.% and the acrylic portion is present
25 form 50-90 wt. %.
5. The water based hybrid alkyd-acrylic latex-of claim 1 wherein the
alkyd portion is present from 20-40 wt.% and the acrylic portion is present
form 60-80 wt. %.

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6. A water-based hybrid alkyd-acrylic latex comprising at least one ethylenically unsaturated monomer having at least one latent oxidative functionality polymerized in the presence of a waterborne alkyd having at least one pendant sulfonate functionality.
- 5 7. The water based hybrid alkyd-acrylic latex of claim 6 wherein the ethylenically unsaturated monomer having at least one latent oxidative functionality is selected from the group consisting of allyl methacrylate, vinyl methacrylate, acetoacetoxyethyl methacrylate, hydroxybutenyl methacrylate, the allyl or diallyl ester of maleic acid, poly(allyl glycidyl ether) and mixtures thereof.
- 10 8. The water based hybrid alkyd-acrylic latex-of claim 6 wherein the alkyd portion is present from 5 to 60 wt.% and the acrylic portion is present from 40 to 95 wt. %.
9. The water based hybrid alkyd-acrylic latex of claim 6 wherein the
- 15 10. The water based hybrid alkyd-acrylic latex of claim 6 wherein the alkyd portion is present from 10-50 wt.% and the acrylic portion is present from 50-90 wt. %.
11. The water based hybrid alkyd-acrylic latex of claim 6 wherein the alkyd portion is present from 20-40 wt.% and the acrylic portion is present from 60-80 wt. %.
- 20 12. An ink formulation comprising the water based hybrid alkyd-acrylic latex of claim 1 and at least one additive.
12. The ink formulation of claim 11 wherein the additive is selected from the group consisting of driers, drier activators, waxes, rheology and flow control agents, extenders, reactive coalescing aids, plasticizers, flattening agents, pigment wetting and dispersing agents and surfactants, ultraviolet absorbers, ultraviolet light stabilizers, tinting pigments, colorants, dyes, defoaming and antifoaming agents, anti-settling, anti-sag and bodying agents, anti-skinning agents, anti-flooding and anti-floating agents, biocides, thickening agents, coalescing agents, and co-solvents.
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13. An ink formulation of claim 11 having improved alkali resistance.
14. An ink formulation of claim 11 having improved gloss.
15. An ink formulation of claim 11 having a volatile organic compound level of less than 25 wt %.
- 5 16. An ink formulation comprising the water based hybrid alkyd-acrylic latex of claim 6 and at least one additive.
17. The ink formulation of claim 16 wherein the additive is selected from the group consisting of driers, drier activators, waxes, rheology and flow control agents, extenders, reactive coalescing aids, plasticizers, flattening agents, pigment wetting and dispersing agents and surfactants, ultraviolet
10 absorbers, ultraviolet light stabilizers, tinting pigments, colorants, dyes, defoaming and antifoaming agents, anti-settling, anti-sag and bodying agents, anti-skinning agents, anti-flooding and anti-floating agents, biocides, thickening agents, coalescing agents, and co-solvents.
- 15 18. An ink formulation of claim 16 having improved alkali resistance.
19. An ink formulation of claim 16 having improved gloss.
20. An ink formulation of claim 16 having a volatile organic compound level of less than 25 wt %.